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Pressurized oxygen blown entrained flow gasification of a biorefinery lignin residue

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ABSTRACT

Renewable fuels could in the future be produced in a biorefinery which involves highly integrated technologies. It has been reported that thermochemical conversion (gasification) of lignocellulosic biomass has a high potential for end production of renewable biofuels. In this work, lignin residue from biochemical conversion of wheat straw was gasified in an oxygen blown pressurized entrained flow gasifier (PEBG) at 0.25–0.30 MWth, $0.45 < \lambda < 0.5$ and 1 bar (g). A video camera mounted inside the PEBG was used to observe the flame during start up and during operation. Hydrogen (H_2), carbon monoxide (CO) and carbon dioxide (CO_2) were the main gas components with H_2/CO ratios varying during the gasification test (0.54–0.63). The methane (CH_4) concentration also varied slightly and was generally below 1.7% (dry and N_2 free). C_2-hydrocarbons (<1810 ppm) and benzene (<680 ppm) were also observed together with low concentrations of hydrogen sulfide (H_2S, <352 ppm) and carbonyl sulfide (COS, <131 ppm). The process temperature in the reactor was around 1200 °C. The slag seemed to consist of Cristobalite (SiO_2) and Berlinite ($AlPO_4$) and Na, Ca, Mg, K and Fe in lower concentrations. Cooling of the burner will be necessary for longer tests to avoid safety shut downs due to high burner temperature. The cold gas efficiency and carbon conversion was estimated but more accurate measurements, especially the syngas flow, needs to be determined during a longer test in order to obtain data on the efficiency at optimized operating conditions. The syngas has potential for further upgrading into biofuels, but will need traditional gas cleaning such as acid gas removal and water gas shifting. Also, higher pressures and reducing the amount of N_2 is important in further work.

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1. Introduction

The EU has set ambitious targets to reduce its overall emissions by at least 20% compared to the 1990s levels by 2020 and to have a renewable energy share of 20% by 2020 [1]. Special attention has been given to development of second generation biofuels [2,3]. Studies have shown that production of biofuels (methanol, DME) via thermochemical conversion (gasification) of lignocellulosic biomass has highest well-to-wheel efficiency among different production pathways [4]. Gasification of biomass results in a synthesis gas mixture mainly composed of carbon monoxide (CO) and hydrogen (H_2) that can be further converted into products [5] such as methanol, H_2, methane (CH_4), gasoline, diesel, dimethyl ether (DME) and ammonia (NH_3). Power production is also possible through the integrated gasification combined cycle (IGCC). Several types of biomass gasifiers exist such as fixed bed reactors, fluidized bed reactors, cyclone and entrained flow gasifiers [6–9]. Entrained flow gasifiers are commercially used with coal as feedstock. A major difference between coal and biomass is the ash composition, which needs special attention since it can melt and cause slagging, attack the reactor containment material or block the reactor outlet. The entrained flow gasifier is fuel flexible and is targeted for oxygen blown, high pressure, high temperature, large capacities applications and has potential for production of a clean essentially tar free syngas. Durability of the containment material due to the high temperature and possible slag will be important to control. In 2011 an entrained flow oxygen blown pressurized biomass pilot gasifier, here denoted PEBG, was built and operated on wood powder [10]. It was found that process temperatures varied between 1100 and 1300 °C with a H_2/CO ratio from 0.54 to 0.57 in the produced syngas and up to 2 % CH_4 was observed in the syngas produced.

Production of a variety of goods from different biomass feedstocks through different technologies may be considered as a biorefinery. The biomass conversion technologies should be highly integrated [11]. Biochemical conversion of lignocellulosic biomass to e.g. ethanol needs a pretreatment step in order to prepare the cellulose to be more accessible for hydrolysis and give high yields in the fermentation step [12]. In this type of processing of the lignocellulosic biomass

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the lignin residue obtained should be further converted to aromatics [11] or used as feedstock to a biomass gasifier [13] to fully utilize the renewable feedstock. Various strategies have been suggested for biomass pretreatment for optimal biomass utilization, but will also result in different degradation products and varying usability of the residues left from the processing [14]. Successful integration of the lignin residue in a biorefinery would also be advantageous for the cellulosic ethanol production cost. Numerous scientific studies in laboratory scale have been reported about lignin gasification [13,15–18]. However, experiences from pilot scale gasification tests of lignin are scarce. In this work we explore the potential for such a lignin residue in the PEBG pilot gasifier. The intended final application of such a process would be production of high value chemicals or biofuels from the bio synthesis gas produced in the gasification process.

2. Experimental

2.1. Lignin preparation

The lignin was produced as a byproduct during biorefinery processing of wheat straw from wheat grown and harvested in Denmark 2011. The initial chemical composition of the wheat straw was 34.5 wt.% lignin, 32.5 wt.% cellulose, 26.4 wt.% hemicellulose, 3.5 wt.% ash and 3.0 wt.% other compounds based on compositional analysis [19]. To prepare the lignin for gasification, the wheat straw was processed by (1) pretreatment, (2) enzymatic hydrolysis and (3) fermentation of free monosaccharides. The pretreatment process was carried out at 163 °C for 15 min in a BioGasol Carbofrac ™ 5D at the premises of BioGasol (Ballerup, Denmark) with sulphuric acid (1 vol.% in the fluidization) as catalyst. The pretreatment was used to keep the lignin in the solid fraction throughout the biomass processing [14]. To continue with enzymatic hydrolysis, the pretreated wheat straw was cooled down and water added to give a total solid content of 20 wt.% and pH was adjusted to pH 5.0 with sodium hydroxide. The enzyme complex used was Cellic CTec2 provided by Novozymes A/S (Bagsværd, Denmark) with a concentration of 50 mg enzyme product per g cellulose as recommended by Novozymes A/S. After 120 h the enzymatically hydrolyzed slurry was transferred to a fermentor, nutrients were added and the yeast (*Saccharomyces cerevisiae*) was inoculated. The fermentation took place for 2 days at 35 °C. Subsequent to the fermentation, the fermentation slurry was separated by a decanter centrifuge and the solid fraction was dried and sent to the Energy Technology Centre in Piteå (Sweden) in two batches where the gasification tests were carried out.

2.2. Characterization and preparation of the lignin for gasification

One sample from each lignin batch was analyzed by external laboratories (ALS Global, Sweden and Belab, Sweden) for ultimate and proximate analysis as well as elemental composition. The material had been thoroughly mixed before sampling. The two lignin batches were milled with a hammer mill (MAFA EU-4B) using a sieve of 0.75 mm. The resulting powders were then characterized for particle size distribution by a Fritsch Analysette 3 sieve instrument and visually observed in a Zeiss Stemi 2000-C optical microscope. The dry content of the mixed lignin powder after milling was 89.5% as measured by a moisture balance (Mettler Toledo HB43 moisture analyzer). Slag samples obtained after the gasification test were analyzed by scanning electron microscopy (SEM) in a Zeiss Gemini Merlin at an accelerating voltage of 20 kV with a thermal field emission source. Energy dispersive spectroscopy (EDS) was carried out with an Oxford Instruments X-Max detector attached to the SEM. A PANalytical Empyrean X-ray Diffractometer equipped with an Empyrean Cu LFF HR X-ray tube, a graphite monochromator and a PIXcel3D detector was used for identification of the slag sample after the gasification test. The slag was crushed in a mortar into a powder before analysis. The HighScore Plus evaluation software and the ICDD PDF database were used for identification of the crystalline phases.

2.3. Gasification of lignin

2.3.1. Description of the pressurized entrained flow biomass gasifier (PEBG)

The PEBG is described in detail elsewhere [10] and only a brief description is presented here. A schematic drawing of the pilot gasification plant is given in Fig. 1. The fuel powder was pneumatically transported from the hammer mill to one of the two hopper storage tanks ($2 \times 1\ m^3$) in the PEBG plant. The PEBG pilot plant, built by Infjärdens Värme AB (IVAB, Sweden), was designed for high process temperatures (1200–1500 °C) and with a thermal throughput of maximum 1 MWth and pressures up to 10 bar (g). The dimension of the PEBG gasifier was 0.52 m (inner diameter) with a length of 1.67 m with a conical shaped outlet. The reactor ceramics, mainly Al_2O_3 (63 wt.%) and SiO_2 (31 wt.%), were slowly heated up (below 100 °C/h in order to avoid thermal stress) to 1000 °C by an electrical heater (Kanthal Tubothal 27 kW) vertically mounted in the centre of the reactor. Thermocouples (Type S, with protective ceramic encapsulation) measured the process temperature at the top, at the middle circumference (120° apart) and at the lower part of the vertical reactor wall according to Fig. 1. The thermocouple tips were mounted coincident with the reactor wall. Note that the temperature in this work is defined as the process temperature measured by the thermocouples and not necessary the real gas temperature [10]. The synthesis gas and solids were cooled and separated in a water quench. The system pressure was controlled by a regulating valve on the syngas outlet pipe after the quench. A water cooled nitrogen purged video camera was used to visualize the flame and the interior of the reactor during the gasification test. After gas sampling, the main syngas stream was sent to a flare on top of the building where an LPG (Liquefied Petroleum Gas) pilot flame was used as a continuous ignition source.

2.3.2. Experimental conditions

Gasification of lignin was targeted at 1 bar (g) with a fuel feeding rate of 55 kg/h, i.e. 0.25–0.30 MWth. The oxygen equivalence ratio, or lambda (λ), defined as the ratio between the supplied oxygen (kg/s) and the stoichiometric oxygen demand (kg/s) for complete combustion, was targeted at 0.45 with an oxygen concentration of 70% of the inlet gas (i.e. 30% nitrogen). The water level in the quench was set to 30%. These parameters were not constant but had to be adjusted slightly during plant operation, which is normal in a pilot plant. In total, 160 kg of lignin was available for the gasification test.

2.4. Gas sampling and analysis

The gas composition, in mol% or mol ppm, was analyzed with respect to CO, H_2, carbon dioxide (CO_2), nitrogen (N_2), oxygen (O_2), CH_4 and ethylene (C_2H_4) using a micro-gas chromatograph, Varian 490-GC (Micro-GC), with two thermal conductivity detectors (TCD). The Micro-GC was connected to the gasifier after the quench and had a cycle time of 3.5 min. Gas samples were withdrawn from the gasifier, using a suction pump. Before entering the chromatograph the gas was filtered using a heated absolute filter to remove particles and cooled through an indirect heat exchanger and filtered through glass wool. Two samples were also collected in 10 dm^3 foil gas sample bags with a single polypropylene septum fitting (SKC). The sample bags were rinsed with N_2 3 times before sampling. The gas samples were analyzed immediately after sampling by a CP-3800 (Varian Inc.) gas chromatograph equipped with two thermal conductivity detectors (TCD) for detection of H_2, CO, CO_2, O_2, C_2H_4, acetylene (C_2H_2) and H_2S. A PFPD (pulsed flame photometric) detector was used for detection of COS and a FID (flame ionization) detector was used for hydrocarbons.

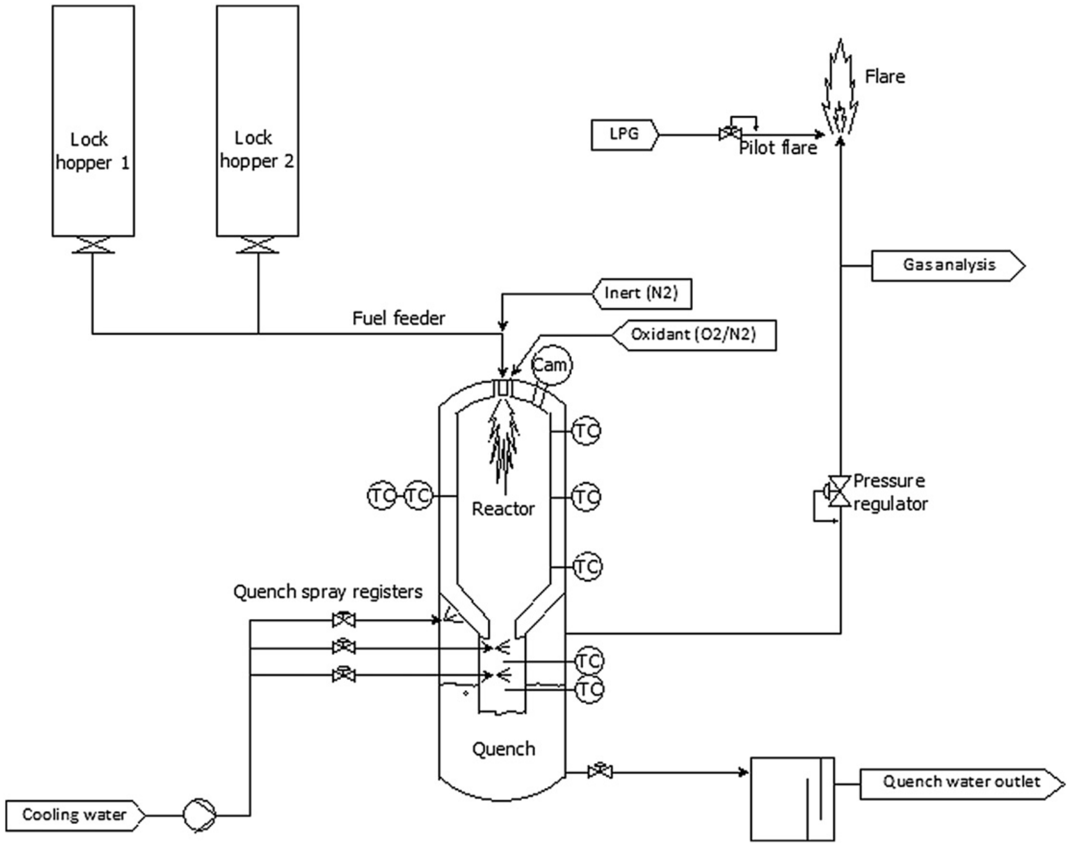

Fig. 1. Schematic drawing of the PEBG plant.

2.5. Estimation of gasifier efficiency

Several criteria exist for evaluating the efficiency of a gasification process [7]. Two common criteria are cold gas efficiency and carbon conversion. The cold gas efficiency is defined here, as in previous work [10], as the ratio between the syngas energy flow (MW) and the energy input (MW) in the corresponding fuel, based on LHV (lower heating value). The carbon conversion is here defined as how much of fuel carbon (kg) is converted to carbon (kg) in the produced gas (CO, CO_2, CH_4, C_6H_6 etc.) during a certain time [10]. Carbon conversion can also be determined from the amount of carbon in the gasification residue, instead of the carbon in the produced gas; however this was not practical in this work.

3. Results and discussion

3.1. Characterization of the lignin

The composition of the solid fraction (the lignin) based on compositional analysis [19] was 47.2 wt.% lignin, 26.2 wt.% cellulose, 6.5 wt.% hemicellulose, 8.4 wt.% ash and 11.7 wt.% of other compounds. In Table 1 the ultimate and proximate analysis results of the lignin samples used for gasification are summarized. Equal amounts of batch 1 and batch 2 were used in the gasification test. Note that the analysis was carried out on the raw material and that minor losses due to volatiles could have occurred during milling and filling to the lock hopper. From the table it can be seen that there is only minor differences between the two lignin samples. The complete elemental analysis of the two samples is given in Table 2. The lignin contained significant amounts of Si (3 wt.%), Na (0.8 wt.%), Ca (0.2 wt.%), K (0.13 wt.%) and Fe (0.1 wt.%) and many other elements at lower concentrations, see Table 2 for details. The ash/slag characteristics was not intended to be studied in detail in this work, it is beyond the scope of this work. However, the fuel sample contain a significant amount of ash/slag forming elements compared to stem wood powder (ash content total 0.4 wt.%) [10]. The effect on the reactor ceramics should be further investigated by e.g. modeling of the smelt formation and by lab scale experiments. The high content of silica indicates a high ash melting point. For coal, the base to acid ratio ($CaO + MgO + Fe_2O_3 + Na_2O + K_2O$)/($SiO_2 + Al_2O_3 + TiO_2$) can give insight in the slagging properties and the base to acid ratios was also evaluated here for the biomass sample. The base to acid ratio was 0.245 for the mixed lignin sample. The slag fluid point T_{25} is between 1380 and 1250 °C [7] at this ratio. The T_{25} temperature is the temperature at which the viscosity is low enough for reliable continuous slag tapping [7]. This means that these temperatures needs to be obtained in order for the slag to flow continuously and not freeze on the reactor wall or in worst case plug the outlet of the reactor.

Table 1
Ultimate and proximate analysis per dry substance of the two lignin samples used for the gasification test.

	Unit	Method	Batch 1	Batch 2
Ash	wt.%	550 °C, SS-EN 14775:2009	10.5	10.9
C fix	wt.%	Calculated	20.8	21.3
Volatiles	wt.%	SS-EN 15148:2009/15402:2011	68.8	67.8
TOC	wt.%	SS-EN 13137 mod.	48.6	48.9
C	wt.%	SS-EN 15104:2011/15407:2011	50.5	50.7
H	wt.%	SS-EN 15104:2011/15407:2011	5.6	5.6
O	wt.%	Calculated	32.1	31.4
N	wt.%	SS-EN 15104:2011/15407:2011	1.0	1.1
S	wt.%	ICP-SFMS	0.29	0.26
Cl	wt.%	SS-EN 15289:2011/15408:2011	0.04	0.04
LHV	MJ/kg	SS-EN 14918:2010/15400:2011	19.3	19.4

Table 2
Elemental analysis per dry substance of the two lignin samples used for gasification test.

	Unit	Method	Batch 1	Batch 2
Si	wt.%	ICP-SFMS	2.748	3.291
Na	wt.%	ICP-SFMS	0.749	0.794
Ca	wt.%	ICP-SFMS	0.156	0.192
K	wt.%	ICP-SFMS	0.116	0.130
Fe	wt.%	ICP-SFMS	0.104	0.076
P	wt.%	ICP-SFMS	0.046	0.047
Al	wt.%	ICP-SFMS	0.022	0.022
Mg	wt.%	ICP-SFMS	0.017	0.020
Ti	wt.%	ICP-SFMS	0.001	0.002
Mn	wt.%	ICP-SFMS	0.001	0.002
Ba	mg/kg	ICP-SFMS	63.2	73.5
Cr	mg/kg	ICP-SFMS	58.3	71.2
Zn	mg/kg	ICP-SFMS	50.3	28.5
Ni	mg/kg	ICP-SFMS	16.3	15.5
Sr	mg/kg	ICP-SFMS	16.1	18.1
Cu	mg/kg	ICP-SFMS	10.4	15.3
Mo	mg/kg	ICP-SFMS	5.2	4.7
Zr	mg/kg	ICP-SFMS	3.71	2.1
W	mg/kg	ICP-SFMS	2.92	3.30
Co	mg/kg	ICP-SFMS	0.793	0.750
Pb	mg/kg	ICP-SFMS	0.526	0.544
Cd	mg/kg	ICP-SFMS	0.0539	0.0580

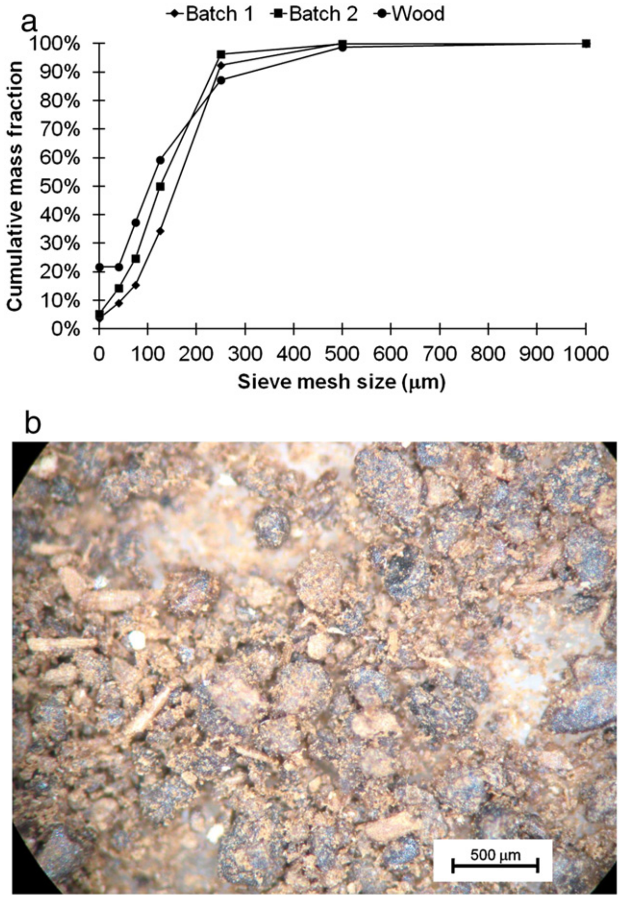

Fig. 2. (a) Particle size distribution for the two lignin samples. (b) Optical microscopy image of the mixed lignin sample after milling.

The energy consumption for milling the lignin was 3.0 kWh_e/MWh_th. Previous experience (unpublished own data) milling ordinary wood pellets (Glommers Miljöenergi, Sweden (GME)) consumed for comparison 15–20 kWh_e/MWh_th for the same equipment and sieve size (0.75 mm). The lignin sample can therefore be considered as an interesting alternative for a powder entrained flow gasifier since the energy for milling is only about 15-20 % of the milling energy needed for wood pellets. For the overall biorefinery energy balance it will of course be important to consider the lignin production including transport to the gasifier when comparing with other fuels such as wood pellets. The particle size distributions for the two samples are shown in Fig. 2(a). For comparison the particle size distribution for the wood sample from GME is also included in the figure. The particle size distributions for the two lignin samples were similar. The lignin samples contain a significant proportion of particles from the 250 µm mesh size. This was confirmed by the visual observation of the mixed lignin sample by optical microscopy which showed dark particles about 0.3-0.5 mm in diameter, see Fig. 2(b). These dark particles appeared to be sticky and smaller brown particles were attached to these and were also observed in-between the larger black particles. Some needle shaped material, appearing to be unreacted straw, was also observed.

In Fig. 3 the characteristics of the lignin fuel is shown with respect to H, C and O content in a van Krevelen diagram. Five other fuels, torrefied wood, peat, rice husk, bark and stem wood are also shown in the figure as a comparison [10,20]. Compared to stem wood the lignin sample has lower H/C and O/C ratios, but not as low as peat. The H/C ratio is similar to a torrefied wood sample. Torrefaction is a thermal treatment (200–300 °C) for improvement of the biomass properties for e.g. combustion and gasification applications [20].

3.2. Gasification test

3.2.1. First gasification period

The first gasification period represents the transient conditions during a start up. The pressure was increased and reached 1 bar (g) after about 8 min and had minor fluctuations at 0.95 bar (g), see Fig. 4(a). The figure also shows that the reactor temperatures steadily increased during the first half of the period, up to around 1200 °C in the top of the reactor, where slagging condition commence, see above. Thus, both non slagging and slagging condition during this test might have occurred. The λ (lambda) was decreased after 36 min from 0.50 to 0.45, which represents the target operating condition. The change in λ resulted in a drop in the temperature as expected, see the figure. After a few minutes of stabilization, the temperatures were more stable from 40 min into the test until the operation was stopped after 64 min. The stop was caused by that the thermocouple temperature close to the burner temperature exceeded the maximum allowable temperature (950 °C). This has occasionally been observed in previous gasification tests in the PEBG with wood powder, but then after long operation time (several hours). Parameters such as fuel load, flame length, lignin reactivity and composition and radiation could explain the higher temperature. This can be overcome in future tests by installing e.g. water cooling

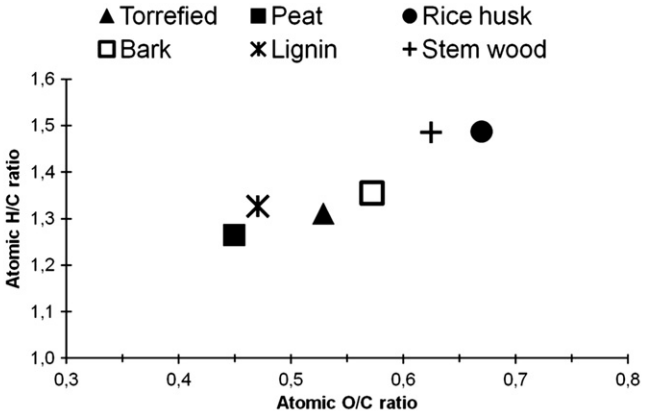

Fig. 3. van Krevelen diagram showing the atomic H/C and O/C ratios for lignin and wood powder. Data for other fuels from [20] is also incorporated for comparison.

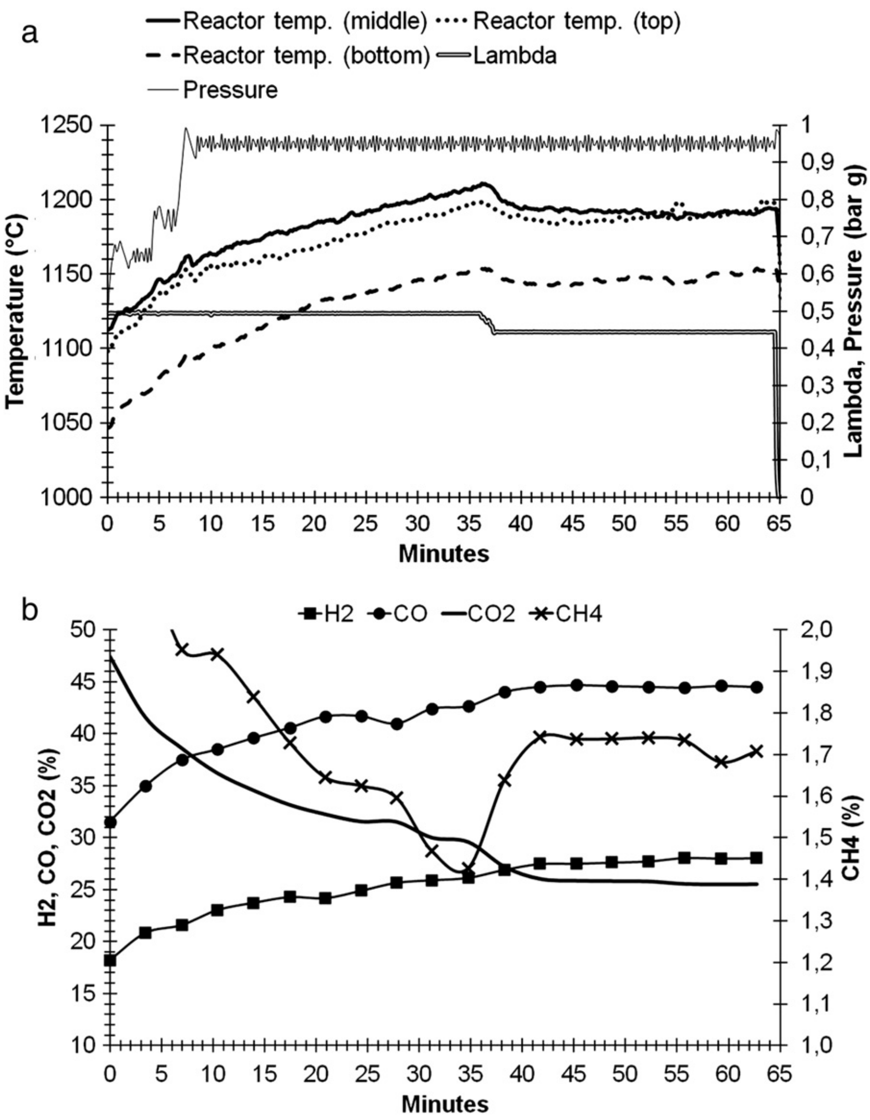

Fig. 4. (a) Reactor temperatures at top, middle and bottom and the λ value and pressure (bar g) during the first gasification period. (b) Gas analysis data from the Micro-GC during the first gasification period.

jacket on the burner. Fig. 5(a)–(d) shows images obtained with the reactor video camera. The electrical heater is shown in (a), (b) shows an image of the reactor during nitrogen purging. The reactor outlet is clearly visible at the upper part of the image. Figures (c) and (d) shows images of the flame with only 0.08 seconds interval. Movement of the flame, probably caused by small variations in the fuel feeding and that the fuel consists of particles with different sizes (see Fig. 2), was observed but any explanation that could explain higher temperature on the burner compared to previous tests with wood powder could not be deduced from the camera recordings.

Fig. 4(b) shows the concentration of the main components H_2, CO, CO_2 and also CH_4 in the first gasification period. Note that these data were normalized excluding both N_2 and O_2. In the experimental tests the N_2 content in the synthesis gas varied as a result of adjustments during operation of the plant. An approximate average N_2 concentration in the synthesis gas was 18%.

The concentrations of both CO and H_2 are increasing initially from 31.5% and 18.2% respectively and seem to reach stable values at the end of the period, similarly as the observed trends for the reactor temperatures. The concentration of CO and H_2 were 44.5% and 28.0%, respectively at the end. The H_2/CO ratio at the end is thus 0.63. CO_2 on the other hand is continuously decreasing from 47 to 25%, especially before the change in λ after 36 minutes. As observed above for the temperatures, the gas composition was also more stable in the second half (from minute 40 to 64) of the operation period.

Minor components were observed in the two gas bag samples; C_2H_4 (550–620 ppm), C_2H_2 (1040–1190 ppm), benzene (C_6H_6, 352–680 ppm), H_2S (340–352 ppm) and COS (129–131 ppm), see Table 3. For comparison, entrained flow gasification of black liquor in a development plant (3 MWth) had similar benzene concentrations (up to about 200 ppm at optimized conditions) but much lower C_2-hydrocarbon content (total 16 ppm) [21]. In drop tube furnace tests the C_2H_2 dominated over C_2H_4 at higher temperatures (>950 °C) [22], which is also observed in these gas samples, see Table 3. Concentrations of benzene and tars from different biomass gasification processes have been summarized [23] and can vary in a broad range depending on type of gasifier and temperature (1–100 g/Nm^3). Generally, the benzene and tar concentration in total can thus vary from around 300 ppm to about 3%.

The gas sample bags (analysis results reported in Table 3) were sampled between 30 and 40 min into the test and the CO concentrations given in the table are in good agreement with the data from the Micro-GC at the corresponding time. Fig. 4(b) shows e.g. that at 30–40 min the concentration of CO was about 44%, which is comparable to the CO concentration given in Table 3. The concentration of H_2

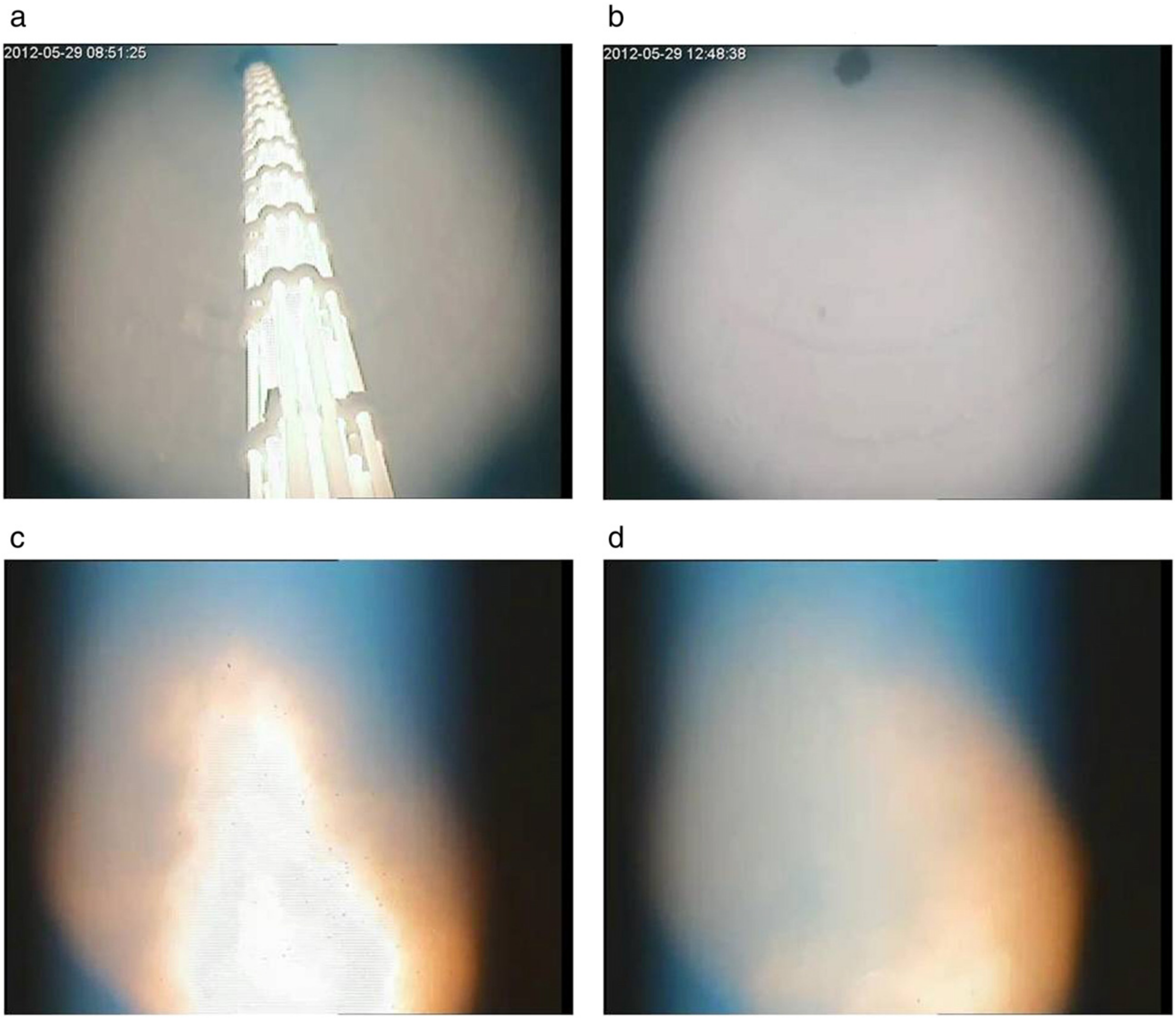

Fig. 5. Images obtained with the camera inside the reactor. Note that there was 0.08 s between (c) and (d).

varies around 25% in the same period as measured by the Micro-GC (Fig. 4(b)) and the corresponding concentration measured from the gas bags were approximately 24%. The CO_2 concentration varied between 31 and 26% as measured by the Micro-GC from 30 to 40 min into the test. The concentration in the gas samples bags were within this range, see Table 3. The H_2/CO ratios for the two samples in Table 3 were thus 0.54. The concentration of CH_4 was slightly lower in the gas sample bag (1.2–1.3%) compared to the concentration measured by the Micro-GC (1.4%, Fig. 4(b)). This could be explained by that especially the CH_4 concentration has a relatively high variation in the time period, see Fig. 4(b). The sudden change in CH_4 concentration after 36 min was caused by the change in λ from 0.50 to 0.45 (see Fig. 4). There is also a significant difference between sampling of gas to the Micro-GC and the gas bag. About 5–10 dm^3 is filled to the gas bag which takes about 30 s followed by analysis on the GC, whereas the Micro-GC analysis analyses a grab sampling every 3.5 min. This might also explain the small difference in H_2 concentration between the gas bag sample and online Micro-GC analysis.

Table 3
Gas composition in mol% and mol ppm for gas sampling bags during the first gasification period. The composition is normalized excluding N_2 and O_2.

	H_2	CO	CO_2	CH_4	C_2H_4	C_2H_2	C_6H_6	H_2S	COS
	%	%	%	%	ppm	ppm	ppm	ppm	ppm
Sample 1	24.0	44.7	29.8	1.3	620	1190	680	340	129
Sample 2	24.3	45.2	29.1	1.2	550	1040	352	352	131

3.2.2. Second gasification period

The reactor temperatures and λ during the second gasification period are given in Fig. 6(a). Similar trends for the H_2, CO and CO_2 concentrations were observed in the first half of the second gasification period as in the first gasification period above. Fig. 6(b) shows again that both H_2 and CO are increasing initially while CO_2 is decreasing. The concentration of H_2 was approximately 27.5%, the CO was 45.5% and the CO_2 was 25% after 65 min. These numbers are very similar to the numbers at the end of the first gasification period above. The H_2/CO ratio after 65 min is thus 0.60 and similar to the ratio observed at the end of the first gasification period above ($H_2/CO = 0.63$ at 64 minutes in Fig. 4(b)).

After approximately 75 and 105 min there were two short stops in the operation of the gasifier, caused by another temperature rise close to the burner. This explains the sudden changes in H_2, CO and CO_2 concentrations in Fig. 6(b) around these times and the dip in temperatures in Fig. 6(a). Abrupt changes can also be seen for the CH_4 and C_2H_4 concentrations given in Fig. 6(c). The concentration of CO is

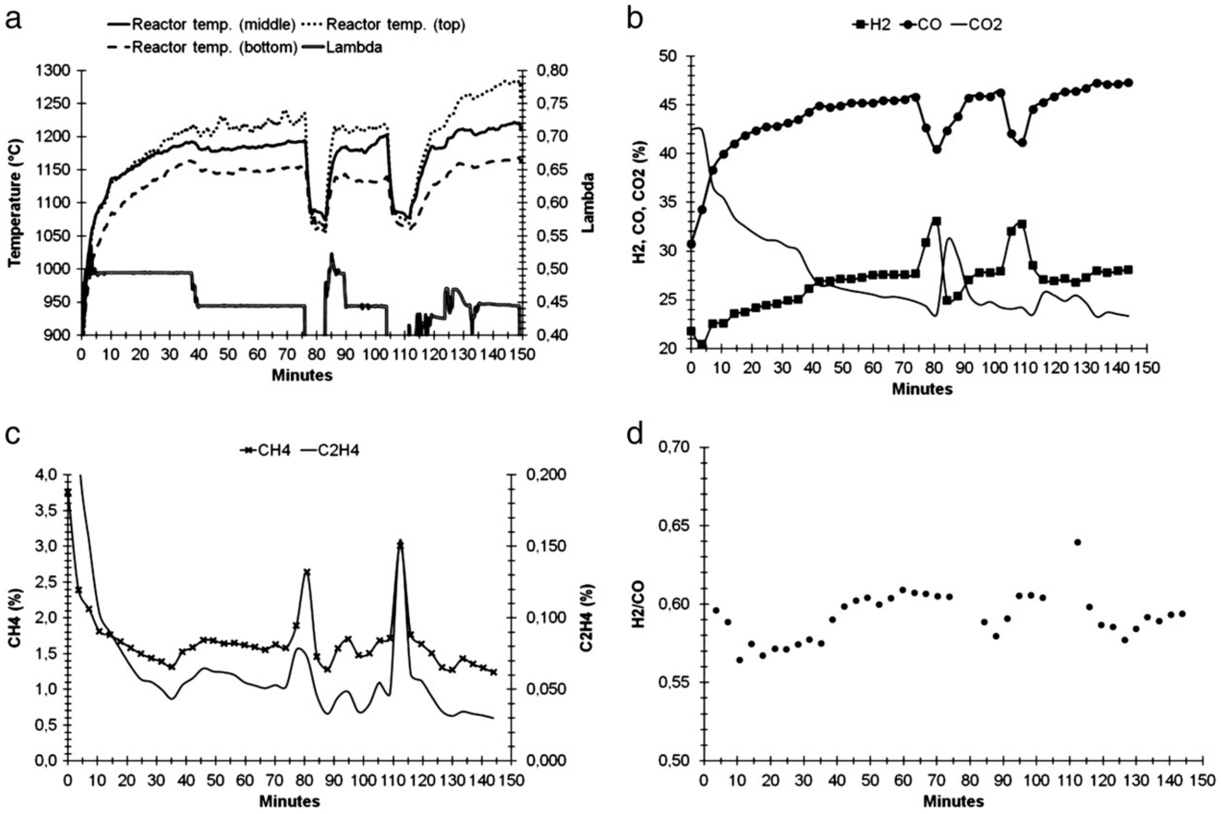

Fig. 6. (a) Reactor temperatures at top, middle and bottom and the λ value during the second gasification period. (b) H_2, CO and CO_2 concentrations as measured by the Micro-GC during the second gasification period. (c) CH_4 and C_2H_4 concentrations as measured by the Micro-GC during the second gasification period. (d) H_2/CO ratio during the second gasification period.

increasing more, up to 47.3% after 144 min and CO_2 is at the same time decreasing further down to 23.3% after the restart at around 115 minutes. The H_2/CO ratio during the second gasification period is shown in Fig. 6(d). The ratio varies only slightly, from about 0.57 to 0.60, except during the temporary stop in the operation of the gasifier at 75 and 105 min. The gasification was stopped after 144 min when the hopper ran out of fuel.

3.2.3. Characterization of slag

From 30 min and to the end of the gasification experiment (144 minutes) the temperature in the top of the reactor was above 1200 °C and about 1275 °C at the end and hence the gasifier was probably in slagging mode in the upper part of the reactor except during the two short stops (trips). The temperature in the bottom was lower, see Fig. 6(a), and non slagging conditions might have occurred in the bottom of the reactor. A white/green/blue and black slag sample was obtained after the gasification test at the quench bottom, see Fig. 7(a). It could not be ensured that the slag stemmed from the lignin alone since gasification with wood [10] and a few other biomass fuels were gasified (unpublished) in the PEBG prior to the lignin for about 200 h. Consequently, it is important to be cautious in the interpretation of the results from slag characterization by e.g. X-ray diffraction or electron microscopy. The SEM-EDS analysis did however show that the slag was mainly composed of Si and O. The slag also contained Na, Ca, Mg, K, P, Fe and Al in lower concentrations, which was also expected from the composition of the ash forming elements in the lignin feedstock. The X-ray diffraction analysis of the slag sample showed presence of Cristobalite (polymorph of silica, ICDD reference pattern 01-082-0512) and Berlinite (polymorph of aluminum phosphate, ICDD reference pattern 01-076-0226) according to the diffractogram that is shown in Fig. 7(b), which correlates well with what was observed in the SEM (rich in Si and O) and to the composition of the feedstock (high Si content). A longer gasification test would be beneficial for detailed slag characterization and then its effect on the reactor ceramics should also be studied in detail. Also, a special slag probe mounted inside the gasifier would be beneficial for investigation of the slag chemistry in future tests.

3.2.4. Potential for upgrading of the synthesis gas

The stoichiometric number $(H_2 - CO)/(CO + CO_2)$ should equal about 2 for methanol synthesis or Fischer–Tropsch synthesis [24–26]. The present synthesis gas from lignin gasification must therefore undergo acid gas removal and water gas shift in order to have proper composition in these conversion pathways. Other products may also be possible to produce from the syngas such as propylene, DME, gasoline, olefins, NH_3 or CH_4 [2,5,27,28]. DME can be produced either by dehydration of methanol or directly from synthesis gas [29,30]. Depending on the engineering technology and catalyst, a H_2/CO ratio from 0.5 to 2 can be used [30]. With respect to the syngas composition from the gasification of lignin in the PEBG, DME could therefore be an interesting choice to consider since the syngas would need less shifting compared to methanol or Fischer Tropsch synthesis. It will be important to further characterize the gas with respect to trace elements since the catalysts used for conversion of synthesis gas are very sensitive to certain elements such as H_2S, COS, halides, alkali metals and metal carbonyls [31–33]. The amount of tars in the gas is also important to determine in future work since they can cause operational problems or deactivation of catalysts [8,21–23,34,35], even if the tar content seem to be low due to the high temperature and relatively low benzene concentrations observed here. Reducing the amount of N_2 added to the gasifier and increasing the pressure is also very important for downstream catalytic conversion and should also be carried out in future work. Depending on biorefinery process layout, plant integration and economics a suitable gas cleaning system [9,36] should be chosen together

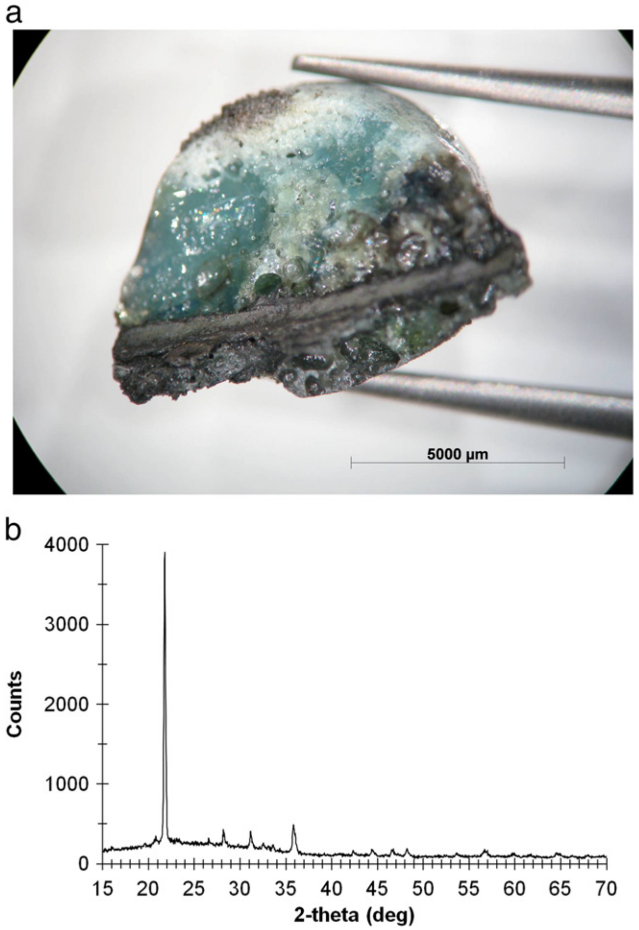

Fig. 7. (a) Optical microscope image of slag obtained at the quench bottom after the gasification test. (b) X-ray diffractogram of the slag sample.

with necessary gas shifting before the synthesis gas is further converted to products.

3.2.5. Estimation of gasifier efficiency

Longer gasification at stable operation would be advantageous, both with respect to fundamental knowledge about the gasification performance but also for determination of the gasification efficiencies. However, in the present work all available lignin was used and the evaluation is thereby limited by results reported here. Future characterization work would require about 1000 kg of lignin but this is a substantial amount of material that needs to be prepared / produced and is beyond the scope of this work.

Calculation of cold gas efficiency and carbon conversion require accurate syngas mass flow measurements. However, this was not achieved and the syngas flow was therefore calculated as reported previously for wood powder gasification tests [10]. The syngas flow was estimated based on the nitrogen content in the syngas and the nitrogen added to the gasifier through the fuel and fuel feeding system, camera and burner. The cold gas efficiency was estimated during minutes 35 to 65 in the second gasification period, as described in ref. [10], to 55 ± 8 %. The error estimations were calculated based on propagation of errors method described elsewhere [37]. The error of the estimated syngas flow was the largest contributing error to the cold gas efficiency and the carbon conversion (see below). The uncertainty of the inlet nitrogen mass flow plays an important role in the propagation of errors. Improving the accuracy of the trace gas mass flow would strongly reduce the experimental error. The cold gas efficiency is reduced by increasing content of N_2 [7]. Reducing the amount of N_2 added through the burner, camera and fuel feeding system will thus increase the cold gas efficiency. Generally, increasing the pressure will increase the cold gas efficiency since the heating value of the produced gas will increase with pressure [7] as a result of CH_4 production through the steam reforming reaction. On the other hand, increasing temperature will decrease the heating value of produced gas and hence lower the cold gas efficiency [7,38]. A produced gas with a high CH_4 content could be used for example power production. However, if the produced gas is intended to be used for catalytic conversion to methanol, DME, Fischer Tropsch products etc, then the yield of H_2 and CO and the H_2/CO ratio should instead be considered [7]. A process with highest cold gas efficiency might not be best choice for biofuel production since the syngas might then need more treatment which in the end will be economically disadvantageous. Thus, the total economic and energy balance must be taken into account when chosing the entire process layout. It is thus important to be careful when interpreting results regarding efficiencies, especially when it comes to uncertainties in pilot scale measurements. Improvements in determining the syngas flow through e.g. flow measurement or by trace experiments will be evaluated in future work as well as optimization of the operation. In ref. [38] different types of fluidized bed biomass gasification tests has been reviewed with reported cold gas efficiencies from 56.9% to 82%. For comparison, saw dust was gasified in an air blown laboratory entrained flow reactor between 700 and 1000 °C and cold gas efficiencies between 37 and 66% were obtained and strongly depended on the operation [39]. Similarly, cold gas efficiencies varied from 20 to 87% in an entrained flow biomass gasifier and depended on addition of steam and air preheating [40].

A comparison of the measured syngas composition in the second gasification (minute 35-65) period with the theoretical composition at equilibrium is presented in Table 4. The composition of the syngas at equilibrium was determined at 1200 °C, 1 bar (g), 70% O_2 and 30% N_2 and $\lambda = 0.45$ for the fuel used here with the FactSage 6.1 computer program. FactSage is an integrated database computing system in chemical thermodynamics. The calculations are performed by determining the minimum of Gibbs free energy of a specific system based on a database containing thermodynamic data for various chemical species and phases. Compared to thermodynamic equilibrium the syngas contains less CO but more CO_2. The syngas also contains 1.6% CH_4 which is not predicted at all at equilibrium ($<10^{-4}$ %).

The carbon conversion was estimated to 86 ± 13%. A carbon conversion of 99% has been achieved for entrained flow processes (coal) [7]. The lower conversion observed here could be explained by the fact that all of the carbon in the fuel was not converted to gas and thereby ends up in the slag and/or the quench water. A possible explanation could be that the heterogeneous reactions involved in char gasification are too slow to be completed within the residence time of the reactor at the current gasification conditions. Therefore, the gas phase is exposed to a higher actual λ value, which promotes the combustion reactions in the gas phase. This will thereby result in more CO_2 and less CO, which could explain the difference between measured CO_2 and CO concentrations compared to equilibrium values. The syngas can also have become shifted in the quench, which could also explain differences between the measured syngas composition after the quench compared to the syngas composition at equilibrium (in the reactor, before the quench). This experimental campaign was the first few hours of experience with gasification of a

Table 4
Average measured syngas composition (mol%, N_2 free, dry gas) from minute 35 to 65 in the second gasification period and corresponding gas composition at equilibrium at 1200 °C.

	H_2	CO	CO_2	CH_4
Measured	27.3	45.1	25.5	1.6
Equilibrium	28.7	56.6	14.5	10^{-4}

lignin fuel in the PEBG and the operating conditions have therefore not yet been optimized. Future work should focus on longer testing (days) and finding optimum operating conditions with 100 % oxygen at higher pressures and investigate the effect of parameter changes such as variation in oxygen equivalence ratio, fuel load and pressure. This would also probably lead to higher carbon conversion and cold gas efficiency with smaller error estimations.

4. Conclusions

Lignin residues from biochemical conversion of wheat straw were gasified in an oxygen blown pressurized entrained flow gasifier at 0.25–0.30 MWth. The experience with gasification of lignin was presented during the initial start up and the first few hours of gasification. A video camera mounted inside the gasifier was used to observe the flame during start up and during operation. Optimization of the process was not possible to carry out in this work; this would need production of a substantial amount of material. H_2, CO and CO_2 were the main gas components with H_2/CO ratios varying during the gasification test (0.54–0.63). The CH_4 concentration also varied slightly and was generally below 1.7% and the benzene concentration was below 680 ppm. C_2-hydrocarbons were also observed together with low concentrations of H_2S (<352 ppm) and COS (<131 ppm). The process temperature was around 1200 °C, which was in the region of slagging condition. The slag seemed to consist of Cristobalite and Berlinite and Na, Ca, Mg, K and Fe in lower concentrations. Cooling of the burner will be necessary for longer tests to avoid safety shut downs due to high burner temperature. The cold gas efficiency and carbon conversion was estimated but more accurate measurements, especially the syngas flow, needs to be determined during a longer test in order to obtain data on the efficiency at optimized operating conditions. Longer tests will also be needed to elucidate the affect on the slag / ash elements on the reactor ceramics.

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